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# PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

## Flexible Wax Coating Compositions

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a wax copolymer composition suitable for coating a substrate.

Wax copolymer blends have been used to coat substrates, for example paper. But, the coating tend to crack and peel when they are repeatedly flexed or severely creased. For packaging wet or grease materials, the blends must give package coatings that will resist grease and water vapour. A wax copolymer composition has now been made which will give coatings having excellent flexibility, grease resistance and water impermeability.

According to the present invention, a composition suitable for coating a substrate comprises 10 to 90% weight of a petroleum wax; 5 to 45% weight of a copolymer of ethylene and a $C_{2-4}$ ester of either a terminally ethylenically unsaturated monocarboxylic acid and a saturated aliphatic alcohol or a terminally ethylenically unsaturated aliphatic alcohol and a saturated monocarboxylic acid, the copolymer having 65 to 85% weight ethylene and 15 to 35% by weight of the ester; and 5 to 45% weight of a wood rosin acid or a glycerol or pentaerythritol ester of the wood rosin acid, the wood rosin acid or its esters providing at least one hydroxy group for each group in the copolymer.

The petroleum wax can be a paraffin, microcrystalline or special wax. Paraffin waxes usually have melting points of about 48 to about 85°C, conveniently about 51 to about 74°C. Examples of the higher melting point paraffin waxes are heavy distillate waxes obtained from the highest boiling distillate lubricating oil fractions by dewaxing. They melt at about 60 to about 85°C, as do high melting point paraffin waxes separated from microcrystalline waxes by fractional crystallisation. Microcrystalline wax (also called amorphous wax) largely has highly branched naphthenic waxes melting about 54 to about 82°C. Special waxes can be obtained by deoiling soft wax fractions normally separated from paraffin waxes during deoiling and dewaxing procedures. Such waxes are very flexible. Different petroleum waxes can be used together, if desired. A convenient mixture is 30 to 55% weight of a distillate paraffin wax having a melting point of 54 to 66°C, 5 to 23% weight of a high melting point paraffin wax having a melting point of 68 to 85°C, and 30 to 55% weight of a microcrystalline wax having a melting point of 54 to 83°C.

Examples of the copolymer are methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, butyl acrylate, and isobutyl acrylate. Preferably, the copolymer is an ethylene vinyl acetate copolymer, which can have 17 to 34% weight vinyl acetate. The ethylene vinyl acetate copolymer preferably has a melt index of 0.2 to 600, especially 0.2 to 10, as found by American Society for Testing Materials (for short ASTM) Method D1238.

Wood rosin acid is of natural origin and as a result is a complex blend of substances. It is a polar resin having hydroxyl groups. According to the present invention, the wood rosin acid and its glycerol and pentaerythritol

esters are chosen such that the wood rosin acid or its esters provide at least one hydroxy group for each ester group in the copolymer.

The composition can be prepared in any conventional way. For example, the components can be mixed together in a molten state with stirring until a homogeneous solution is obtained. The components can be used in any order and concentration, according to the application desired. For example, an excellent hot melt adhesive has 20% weight petroleum wax, 40% weight copolymer, and 40% weight rosin acid or rosin ester. Such a composition has a high content of copolymer and rosin acid or rosin ester. It can serve a a concentrate for transport, and can be diluted with petroleum wax to give a desired concentration of copolymer and rosin acid or rosin ester. Other convenient compositions have 60 to 90% weight petroleum wax, to 5 to 20% weight copolymer, and 5 to 20% weight rosin acid or rosin ester. When a composition of the invention is used as an adhesive, the total wax concentration can be at most 50% weight. When used as a coating composition, the concentration of copolymer and rosin or rosin ester can be less than 50% weight, preferably 10 to 40% weight.

Compositions of the invention can be used for coating different substrates, for example paper, paperboard, and metal surfaces. For coating a metal surface, it may be desirable to add above 5 to 15% weight of polyethylene to the composition. For example, the composition can have 40% weight petroleum wax, 25% weight ethylene vinyl acetate copolymer, 25% weight of a wood rosin acid, and 10% weight polyethylene.

The invention will now be illustrated by the following Examples.

## EXAMPLE I

A concentrate was prepared by blending together in a molten state 40% weight of an ethylene vinyl acetate copolymer containing 24 to 26% weight vinyl acetate and having a melt index of 1.6 to 2.4, 40% weight of pentaerythritol ester of a wood rosin acid having a mol ratio of 1.22/1 of hydroxy groups to ester groups in the copolymer, and 20% weight of a petroleum wax. The wax was a mixture of 43% weight of a distillate paraffin wax having a melting point of about 61°C, 14% weight of a paraffin wax having a melting point of about 70°C and 43% weight of a microcrystalline wax having a melting point of about 80°C. The concentrate was blended together in a molten state into a homogeneous solution. A portion of the concentrate was then applied as a hot melt between two fibrous substrates, and upon cooling was found to possess excellent adhesive properties.

## EXAMPLE II

The concentrate prepared in Example I was diluted with varying amounts of the wax used in Example I. Sufficient wax was added to the concentrate to form blends having a total copolymer plus rosin ester concentration of 15% weight, 24% weight and 30% weight. These blends were used to coat corrugate board in a curtain coating operation. Properties of the blends and coated corrugate board are in Table I below.

TABLE I

| Blend | 1 | 2 | 3 |
|---|---|---|---|
| Copolymer, % weight | 7.5 | 12 | 15 |
| Pentaerythritol ester of wood rosin acid, % weight | 7.5 | 12 | 15 |
| Flow point, °C. | 70 | 70 | 70 |
| Viscosity, cps. | | | |
| 121°C. | 95 | 350 | 850 |
| 149°C. | 65 | 180 | 450 |
| 176°C | 45 | 95 | 240 |
| Scuff resistance | good | very good | excellent |
| Flexibility | good | very good | excellent |
| Adhesion to substrate | good | very good | excellent |
| Gloss | good | good | good |
| Coefficient of friction (a) | 0.53 | 0.54 | 0.54 |
| Slip on tilting table | 27—32° | 27—32° | 27—32° |
| Grease resistance, hours (b) | >240 | >240 | >240 |
| WVTR gm/100 in²/24 hours (c) 37.8°C. 95% R.H. | | | |
| Flat | 0.6 | 0.5 | 0.4 |
| Folded score | 0.7 | 0.9 | 0.7 |

(a) Sliding block.

(b) Raw bacon

(c) Corrected to 1 mil thickness

The above results show a 30% weight copolymer and rosin ester concentration gave the best overall results, but all three blends had excellent flexibility, scuff resistance, adhesion to substrate, grease resistance, and water vapour impermeability.

The comparisons in Table I are for the same blends at varying polymer concentrations. The designations "excellent", "very good" and "good" are therefore relative terms using the 30% weight polymer rosin ester as reference. It will be shown below that even when the 7.5% weight copolymer and 7.5% weight rosin ester blend is compared to a comparable blend not containing the wood rosin ester that the wood rosin ester blend will possess superior properties when compared to the blend without the wood rosin ester.

EXAMPLE III

To demonstrate the criticality of using the appropriate ratio of copolymer to rosin ester, a wax-copolymer-rosin ester blend containing 15% weight ethylene-vinyl acetate copolymer described in Example I, 10% weight of a pentaerythritol ester of a wood rosin acid having a mol ratio of 0.51/1 of hydroxy groups to ester groups in the copolymer, and 75% by weight of the petroleum wax of Example I was applied to a corrugated box

as a coating. When the coating was folded at 180°, severe cracking and breaking of the coating occurred indicating lack of flexibility.

EXAMPLE IV

To show the superior flexibility of wax blends containing both the above-described copolymers and wood rosin esters, the following comparisons were made utilising only the wax of Example I and a copolymer of ethylene and an ethylenically terminally unsaturated ester. The results are in Table II below.

TABLE II

| Blend | 4 | 5 | 6 | 7 |
|---|---|---|---|---|
| Copolymer | 7.5 (a) | 12.0 (a) | 15.0 (a) | 15.0 (b) |
| Wax | 92.5 | 88.0 | 85.0 | 85.0 |
| Scuff resistance | Poor | Fair | Fair | Good |
| Flexibility | Poor | Poor | Poor | Poor |
| Adhesion to substrate | Good | Good | Good | Good |
| Grease resistance, hours (c) | >240 | >240 | >240 | >240 |
| WVTR gm/100 in /24 hours (d) | | | | |
| 37.8°C., 95% R.H. | | | | |
| Flat | 0.3 | 0.5 | 0.5 | 0.6 |
| Folded score | 1.3 | 0.9 | 1.0 | 1.2 |

(a) Ethylene-vinyl acetate copolymer having 24 to 26% weight vinyl acetate, melt index 1.6 to 2.4.

(b) Ethylene-isobutyl acrylate copolymer having 30% weight isobutyl acrylate, melt index 263.

(c) Raw bacon.

(d) Corrected for 1 mil film.

As noted in Table II, the flexibility of each of blends 4 to 7 was poor compared with blend 3 of Table I. The scuff resistance of blends 4 to 7 was also notably inferior and the adhesive properties only mediocre. It is not the amount of total polymer in blends 1 to 3 that provides their excellent flexibilities. For example, compare blends 6 and 7 (each has 15% weight copolymer) with blend 1 (which contains 7.5% weight rosin ester). Blend 1 containing the wood rosin ester has much better flexibility than the blends containing the same total amount of polymer but not the rosin ester.

EXAMPLE V

A blend similar to blend 7 was prepared with the exception that only 70% weight wax was used with 15% weight of ethylene-isobutyl acrylate copolymer and 15% weight pentaerythritol ester of a wood rosin acid having a mol ratio of 1.5/1 of hydroxy groups to ester groups in the copolymer. This blend possessed very good flexibility, good scuff resistance, and good adhesion to substrate.

WHAT WE CLAIM IS:—

1. A composition suitable for coating a substrate, comprising 10 to 90% weight of a petroleum wax; 5 to 45% weight of a copolymer of ethylene and a $C_{3-7}$ ester of either a terminally ethylenically unsaturated monocarboxylic acid and a saturated aliphatic alcohol or a terminally ethylenically unsaturated alcohol and a saturated monocarboxylic acid, the copolymer having 65 to 85% weight ethylene and 15 to 35% weight of the ester; and 5 to 45% weight of a wood rosin acid or a glycerol or pentaerythritol ester of the wood rosin acid, the wood rosin acid or its esters providing at least one hydroxy group for each ester group in the copolymer.

2. A composition as claimed in claim 1, in

which as the wax there is 30 to 55% weight of a distillate paraffin wax having a melting point of 54 to 66°C, 5 to 23% weight of a high melting point paraffin wax having a melting point of 68 to 85°C, and 30 to 55% weight of a microcrystalline wax having a melting point of 54 to 83°C.

3. A composition as claimed in claim 1 or 2, in which there is a copolymer of ethylene and methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, butyl acrylate or isobutyl acrylate.

4. A composition as claimed in claim 1 or 2, in which there is a copolymer of ethylene and vinyl acetate.

5. A composition as claimed in claim 4, in which the copolymer of ethylene and vinyl acetate has 17 to 34% weight ethylene.

6. A composition as claimed in claim 4 or 5, in which the copolymer of ethylene and vinyl acetate has a melt index (ASTM D1238) of 0.2 to 600.

7. A composition as claimed in claim 6, in which the copolymer of ethylene and vinyl acetate has a melt index (ASTM D1238) of 0.2 to 10.

8. A composition as claimed in any one of claims 1 to 7, in which there is a pentaerythritol ester of a wood rosin acid.

9. A composition as claimed in claim 1, substantially as described in any one of the Examples.

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